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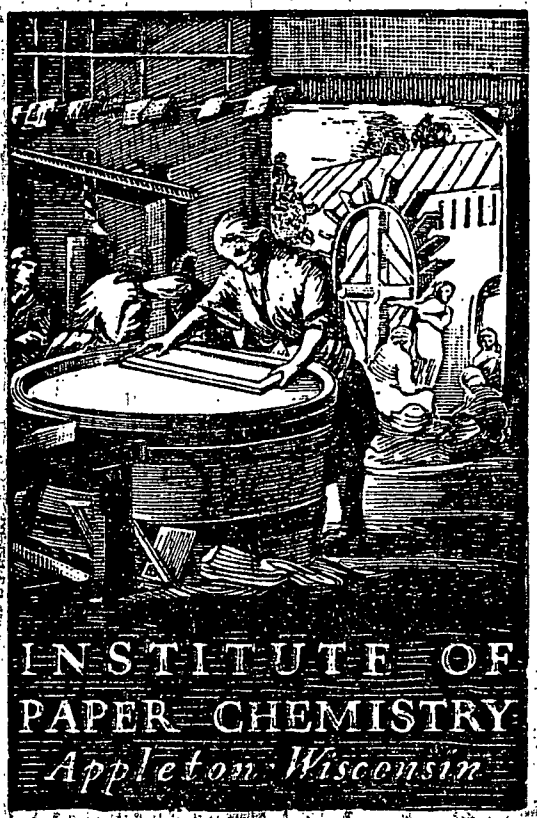

INVESTIGATION OF THE RELATIONSHIP BETWEEN LIGNIN STRUCTURE AND ITS MECHANICAL AND ADHESIONAL BEHAVIOR

Project 2421

Report Nine

A Progress Report

PULP MANUFACTURERS RESEARCH LEAGUE

April 25, 1969

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

In examining further the surface chemical properties of lignosulfonates as related to their utilization as plywood adhesives, the critical surface tension (γ_c) of southern pine veneer, both springwood and summerwood, was determined as a function of aging of the surface. The results show a decline in γ_c from 39-40 dynes/cm. for freshly generated surfaces to 27-29 dynes/cm. for surfaces aged two weeks at 73°F. and 50% R.H. In general, the summerwood proved to be of slightly lower γ_c than the springwood. Layups were subsequently formed from freshly generated and aged veneer surfaces utilizing unmodified electrodialyzed lignosulfonic acids (ELSA) and a formulated adhesive containing ELSA. While the bond strength values were quite irregular within a given series, the formulated adhesive provided roughly twice the bonding strength of the unmodified ELSA and a trend for reduced strength was indicated among surfaces aged two weeks. Inspection of the ruptured specimens indicated that failure in samples bonded with unmodified ELSA was 80-90% cohesional (within the adhesive) whereas failure in specimens bonded with the formulated adhesive was 50-90% within the wood. In general, wood failure tended to decrease as the veneer was aged, suggesting that freshly generated surfaces provide better adhesion. This observation is in agreement with the measured differences in critical surface tension and with practical bonding experience. Means to modify the ELSA adhesive to improve adhesion on the aged veneer surfaces will be examined in subsequent studies.

In the project area dealing with the cohesional strength of lignosulfonic acid adhesive materials for plywood, work on the improvement of ELSA wettability and on the suitability of reed substrates was done.

In order to eliminate orientation of low surface energy molecules as a cause of the release of the ELSA material on drying on a once wetted surface, the potentially troublesome low molecular weight materials were removed (1) by extracting ELSA with reagent-grade ether, or (2) by fractionation with a gel permeation column. Samples of materials prepared by both methods were placed on a variety of potential reed substrates and were examined for cracking and release as they dried. The substrates tested included aluminum, glass, cellulose acetate, Dacron, Nylon, Papylon, Millipore filter, polyolefins, cellophane, Mylar, asbestos, rubbers, and paper. The behavior of these extracted or fractionated ELSA appeared to be no different than the whole ELSA. Thus, orientation of low molecular weight fractions does not seem to be the cause of loss of wettability. However, no adhesional loss was apparent when a porous or very rough substrate was used.

Reeds were cut from 6 x 6 in. layups made from the potentially useful substrates, red rubber, fiber glass filter, Mylar, and kraft paper (linerboard, 149 lb. per TAPPI ream), using a sodium base, heat-treated ELSA cured at 310°F. for 30 min. and 150 p.s.i. The Mylar and the red rubber layups were poorly bonded and, therefore, not useful. The kraft paper was selected for further reed work because of its relatively low loss tangent and its close relationship to wood. In a similar manner, reeds were prepared using an ammonium-base ELSA; an ammonium-base LSA; an ether-extracted, sodium-base ELSA; phenol-formaldehyde; and an ELSA-phenol-formaldehyde-wood meal formulation. Reed vibrational data were obtained. The phenol-formaldehyde and the formulation are good adhesives and, as anticipated, had the highest average loss tangent. However, the range of values from paper only to the best bonded reed was small (0.024-0.050) and the scatter about each average was high (up to $\pm$ 50%) so that valid trends are not yet possible to discern. The use of lighter weight paper in order to maximize the contribution of the adhesive to the measurements

will be studied next. In addition, quantitative measurements of bond strength will be made so that correlation of these with viscomechanical properties can be examined.

Surface tensions of the above adhesive were determined by means of a DuNouy tensiometer. They ranged from 42.9 to 56.7 dynes/cm. with the phenol-formaldehyde adhesive having the highest value. Considering the lower critical surface tension of wood surfaces, bonding may be accomplished, at least in part, by mechanical linkages. Improvement of wetting may improve adhesion performance.

ADHESIONAL PROPERTIES OF LIGNOSULFONIC ACIDS

INTRODUCTION

This is Progress Report Nine on Project 2421 describing results obtained in extended studies concerned with the adhesional and cohesional properties of lignosulfonates as related to their utilization as plywood ahesives.

By way of review, it was previously shown (1) that whole electrodialyzed lignosulfonic acid (ELSA) liquors from the same source and fractions derived from the same whole liquor differed in surface tension and, hence, in the ability to wet and adhere to a given solid surface. The ELSA fractions ranged in surface tension from 38 to 53 dynes/cm.; however, only the lowest molecular weight fraction, representing a mere 4.3% of the total weight, possessed a surface tension lower than that of the whole liquor. A cursory examination of southern pine veneer surfaces (considered the most difficult wood surface to bond) indicated that the wettability of the surface declined with aging at room temperature and had reached a critical surface tension (γ_c) of approximately 32-33 dynes/cm. after six days. According to the chemical theory of adhesion (see Introduction, Report Seven), none of the whole liquors or fractions would be capable of spreading on, and adhering to, the aged veneer surface since, in order for adhesion to occur, the surface tension of the adhesive must be equal to, or less than, the critical surface tension of the substrate. However, the critical surface tension of the freshly generated surface was not measured because of the rapid penetration of the reference liquids. Hence, the ability of the ELSA liquors to wet such surfaces was not established satisfactorily. It was proposed, therefore, to extend these studies to permit more accurate measurement of γ_c for southern pine veneer surfaces and to correlate these studies with practical bonding

strength measurements. Ultimately, means to improve the adhesional behavior of the lignosulfonates were to be explored.

EXPERIMENTAL

Surface Chemical Properties of Southern Pine Veneer

A fresh supply of hot peeled clear southern pine veneer (50 x 50 x 1/8 inch) was obtained from the Southern Pine Plywood Company for the experimental program. In preparation for critical surface tension measurements, strips approximately 1/2 x 6 inches were cut from the veneer. The strips were placed in a holder and were sanded first with a medium weight abrasive paper (C-weight) followed by a finish weight (A-weight). Dust was removed from the surfaces by vacuuming. The Bendtsen smoothness (air escape) of samples processed in this manner fell in the range of 2600-3200 ml./min.

Contact angle measurements utilizing butanol-water mixtures were made on freshly sanded surfaces and on samples which had aged for 4, 8, 16, 48, 96, 264, and 360 hours at 73°F. and 50% R.H. An effort was made to use halogenated hydrocarbons in place of butanol-water but these materials penetrated instantaneously. Measurements were made on both springwood and summerwood areas with a contact angle goniometer equipped with a 35-mm. Leica still camera and a Micro-Ipso adaptor. The film used was Pan Film Plus X and the shutter speed was 1/50 second. The drop size was approximately six microliters. The contact angles were measured directly from the photographs and the results are recorded in Table I.

The critical surface tension of the veneer surfaces was determined from the intercept of the cos θ *vs.* surface tension (γ_L) plot with the cos θ = 1 axis. The plots for the various aging intervals are presented in Fig. 1-8. (Note: the slope and intercept of these lines were determined from regression coefficients).

TABLE I

CONTACT ANGLE DATA FOR SOUTHERN PINE VENEER SURFACES

Butanol Concn. by Wt.	Surface Tension (γ_L), dynes/cm.	Contact Angle θ, degrees after aging															
		0 hr.		4 hr.		8 hr.		16 hr.		48 hr.		96 hr.		264 hr.		360 hr.	
		Spring-wood	Summer-wood	Spring-wood	Summer-wood	Spring-wood	Summer-wood	Spring-wood	Summer-wood	Spring-wood	Summer-wood	Spring-wood	Summer-wood	Spring-wood	Summer-wood	Spring-wood	Summer-wood
0.25	65.7	66	74	--	--	80	83	79	68	--	--	81	--	--	--	--	--
0.50	60.8	58	63	62	68	82	84	67	69	--	79	76	77	--	85	--	--
0.75	57.1	62	60	--	--	72	67	59	61	--	76	75	71	80	82	--	--
1.00	53.4	40	40	50	55	64	64	--	65	70	72	--	69	76	75	75	73
1.50	48.9	41	46	53	55	55	61	--	55	62	62	58	68	--	72	67	70
2.00	45.4	27	30	43	46	--	--	41	45	--	54	53	57	65	59	62	62
3.00	42.5	25	30	27	25	34	42	39	43	52	45	40	48	--	57	60	62
3.50	38.2	--	--	--	--	--	--	--	34	30	29	--	36	43	49	44	45
4.00	36.3	--	--	--	--	--	--	21	26	20	--	--	--	35	37	37	42
4.50	34.4	--	--	--	--	--	--	15	--	18	--	--	--	31	37	35	35

Note: The contact angles listed above represent the average of 2-4 readings.

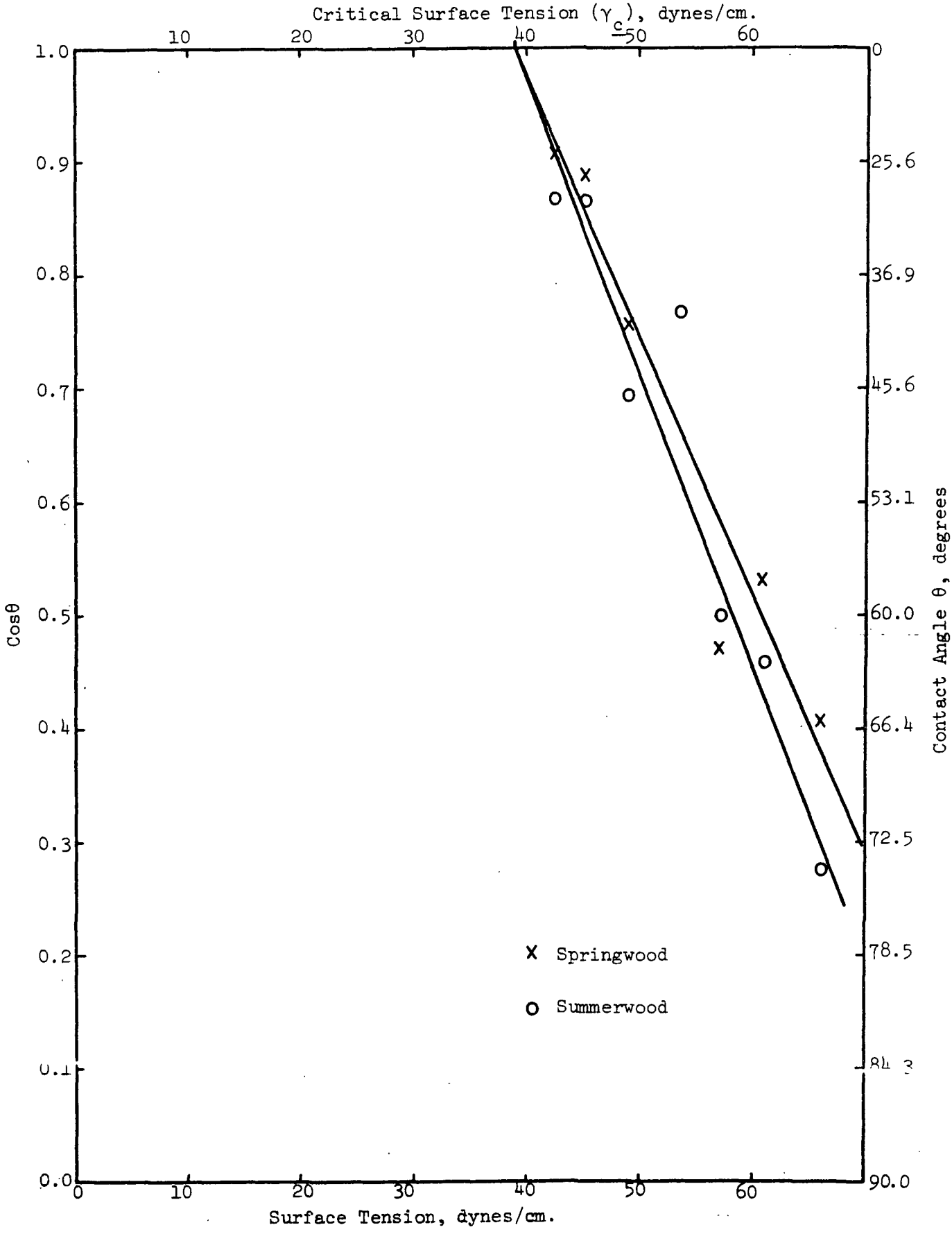

Figure 1. Cosθ — Surface Tension Relationships for Freshly Generated Southern Pine Veneer Surfaces

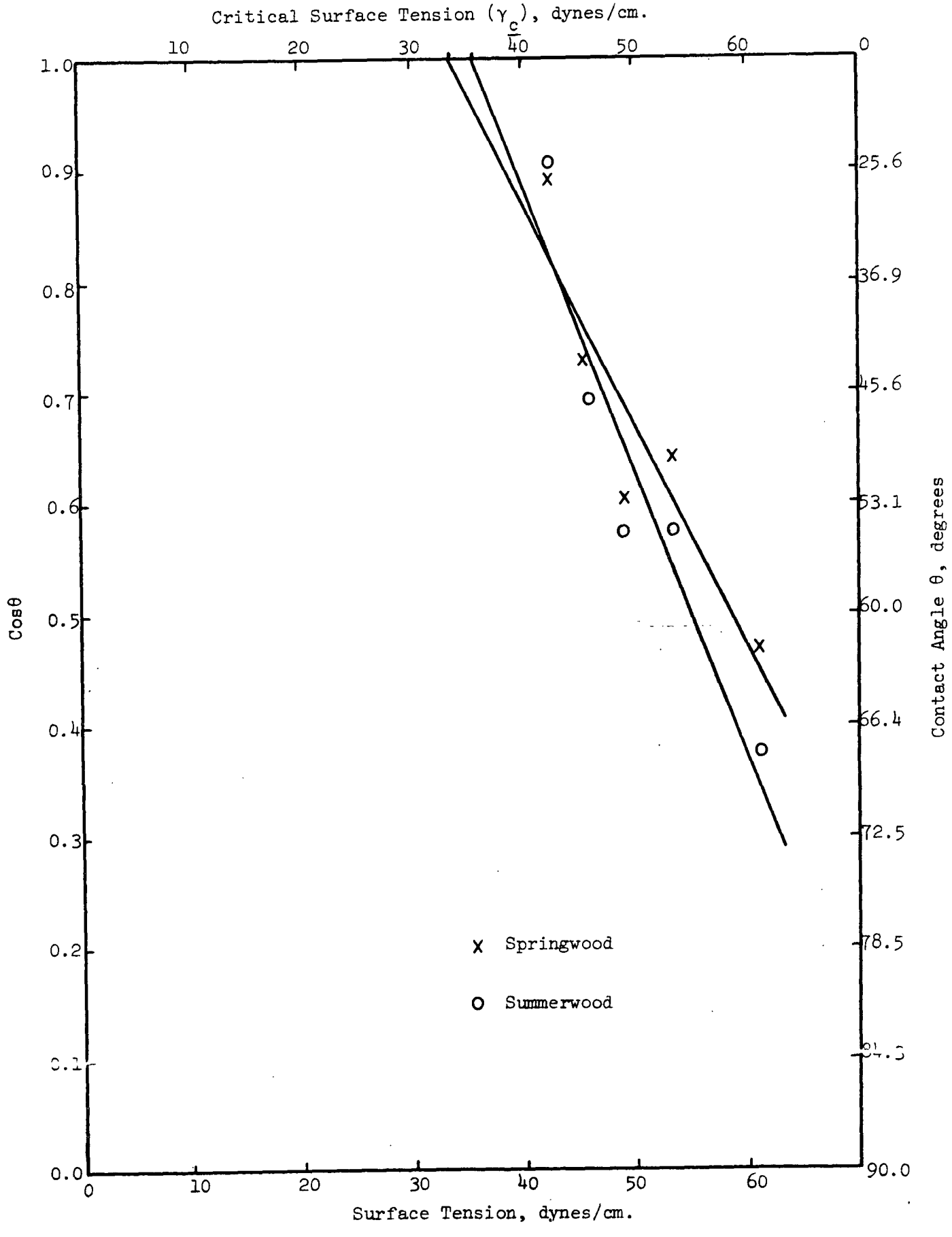

Figure 2. Cosθ — Surface Tension Relationships for Southern Pine Veneer Surfaces Aged Four Hours

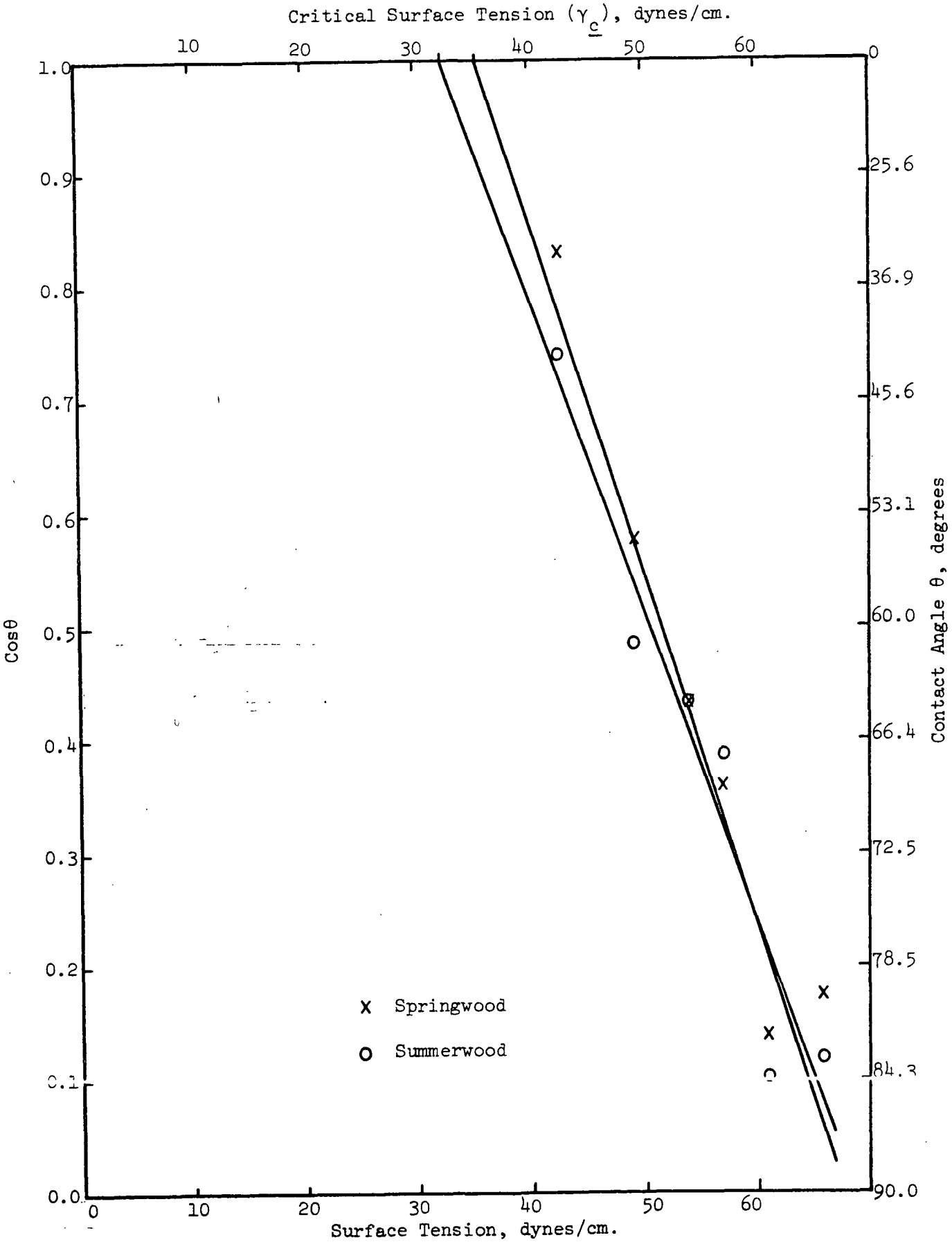

Figure 3. Cosθ — Surface Tension Relationships for Southern Pine Veneer Surfaces Aged Eight Hours

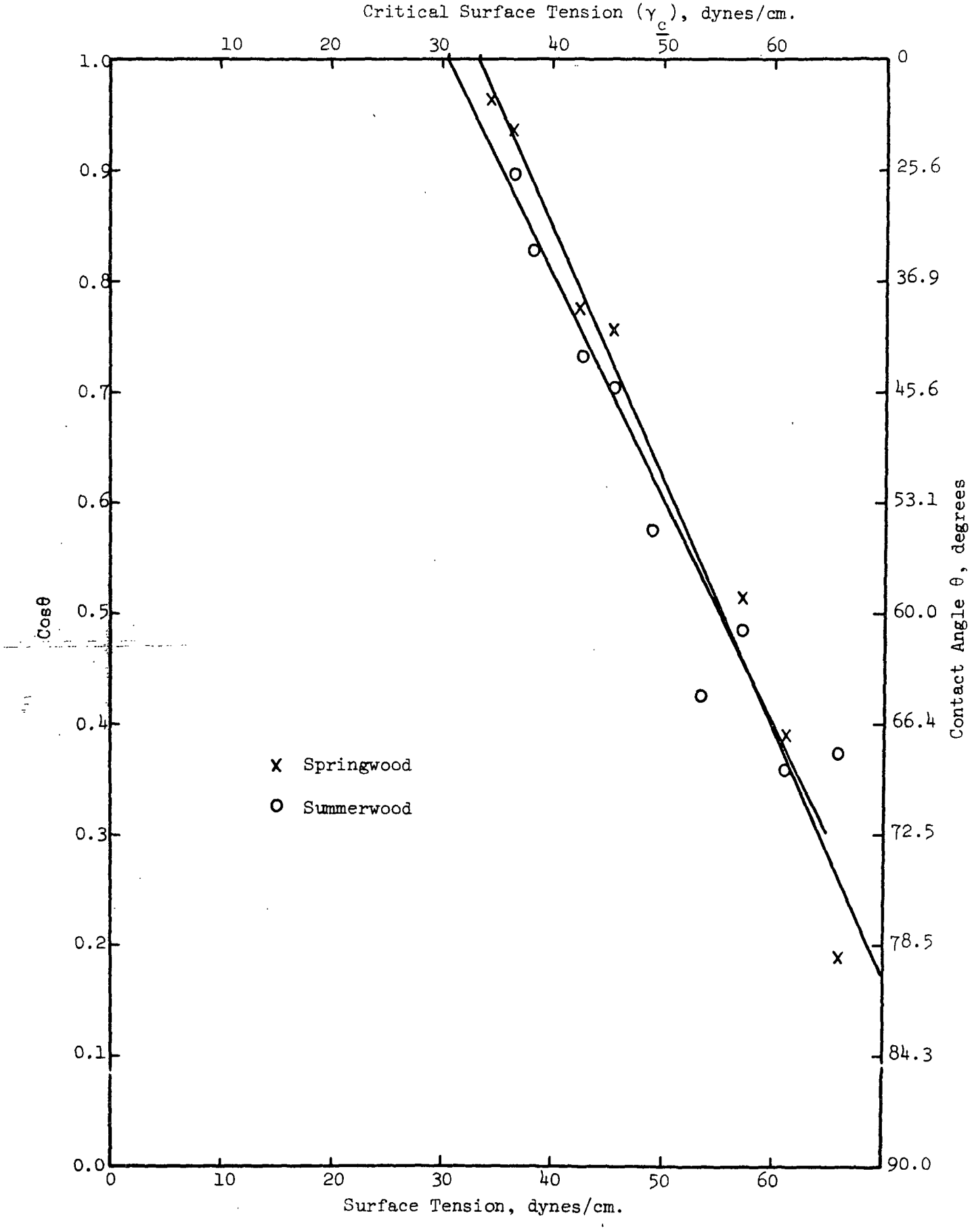

Figure 4. Cosθ – Surface Tension Relationships for Southern Pine Veneer Surfaces Aged 16 Hours

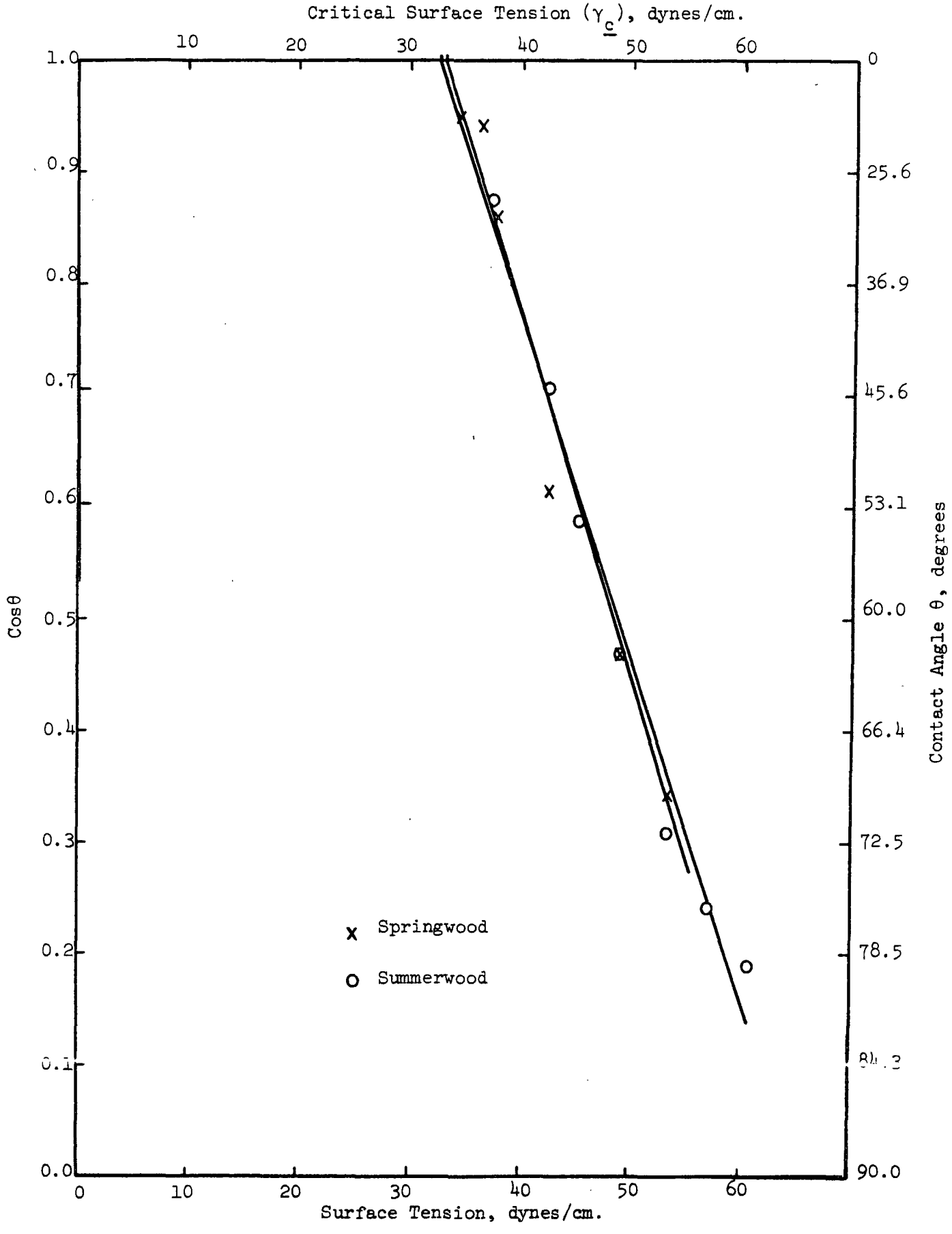

Figure 5. Cosθ — Surface Tension Relationships for Southern Pine Veneer Surfaces Aged 48 Hours

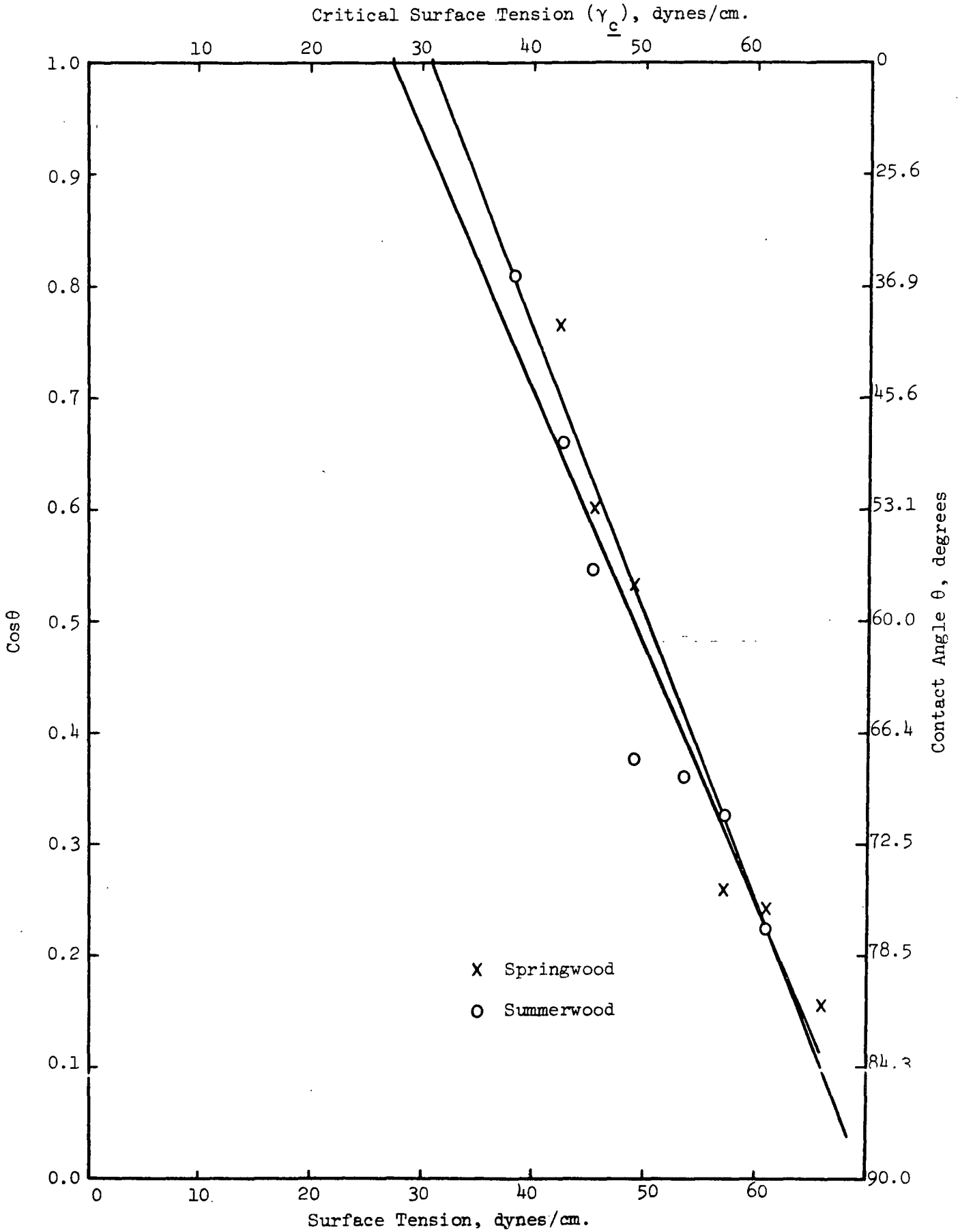

Figure 6. Cosθ — Surface Tension Relationships for Southern Pine Veneer Surfaces Aged 96 Hours

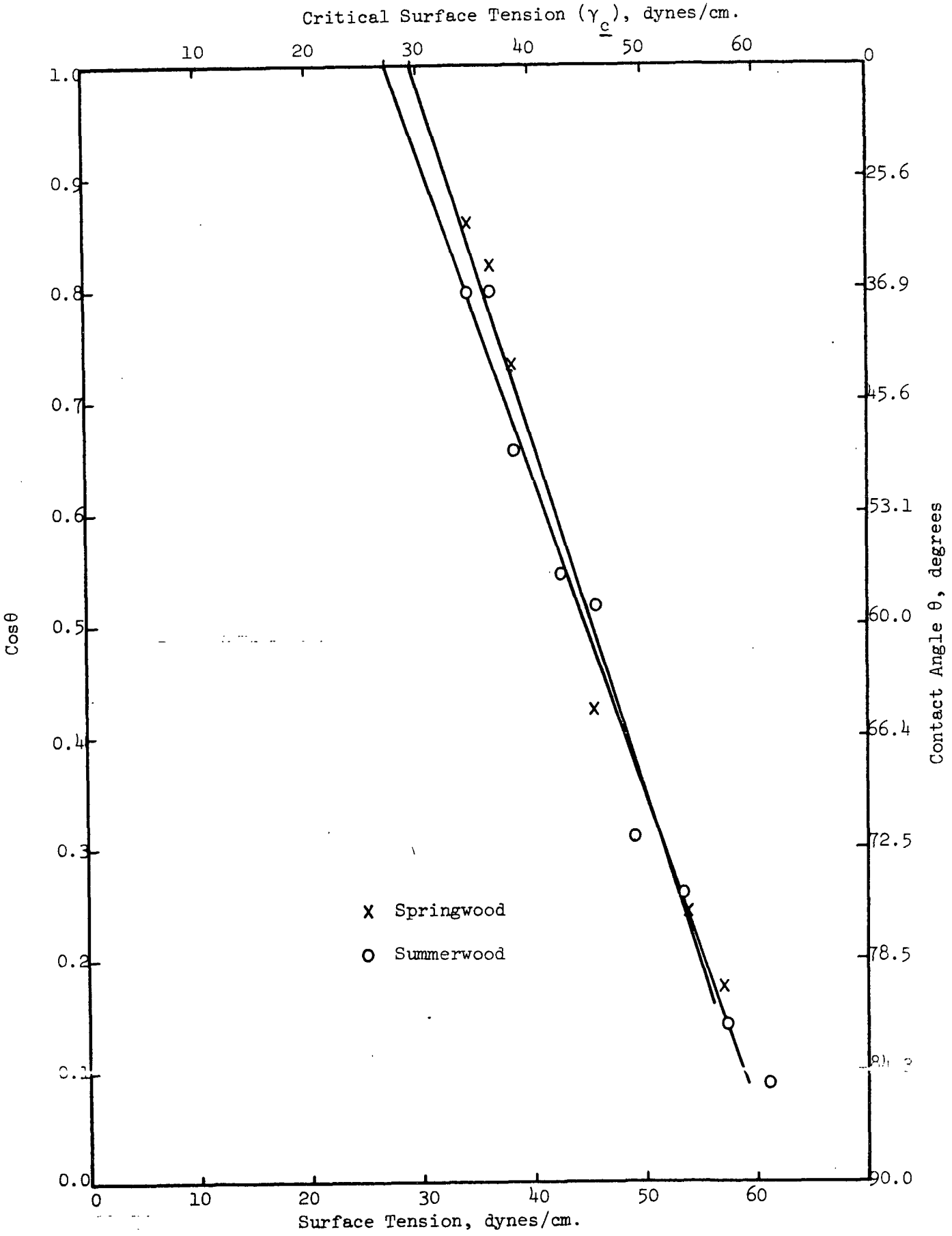

Figure 7. Cosθ — Surface Tension Relationships for Southern Pine Veneer Surfaces Aged 264 Hours (11 Days)

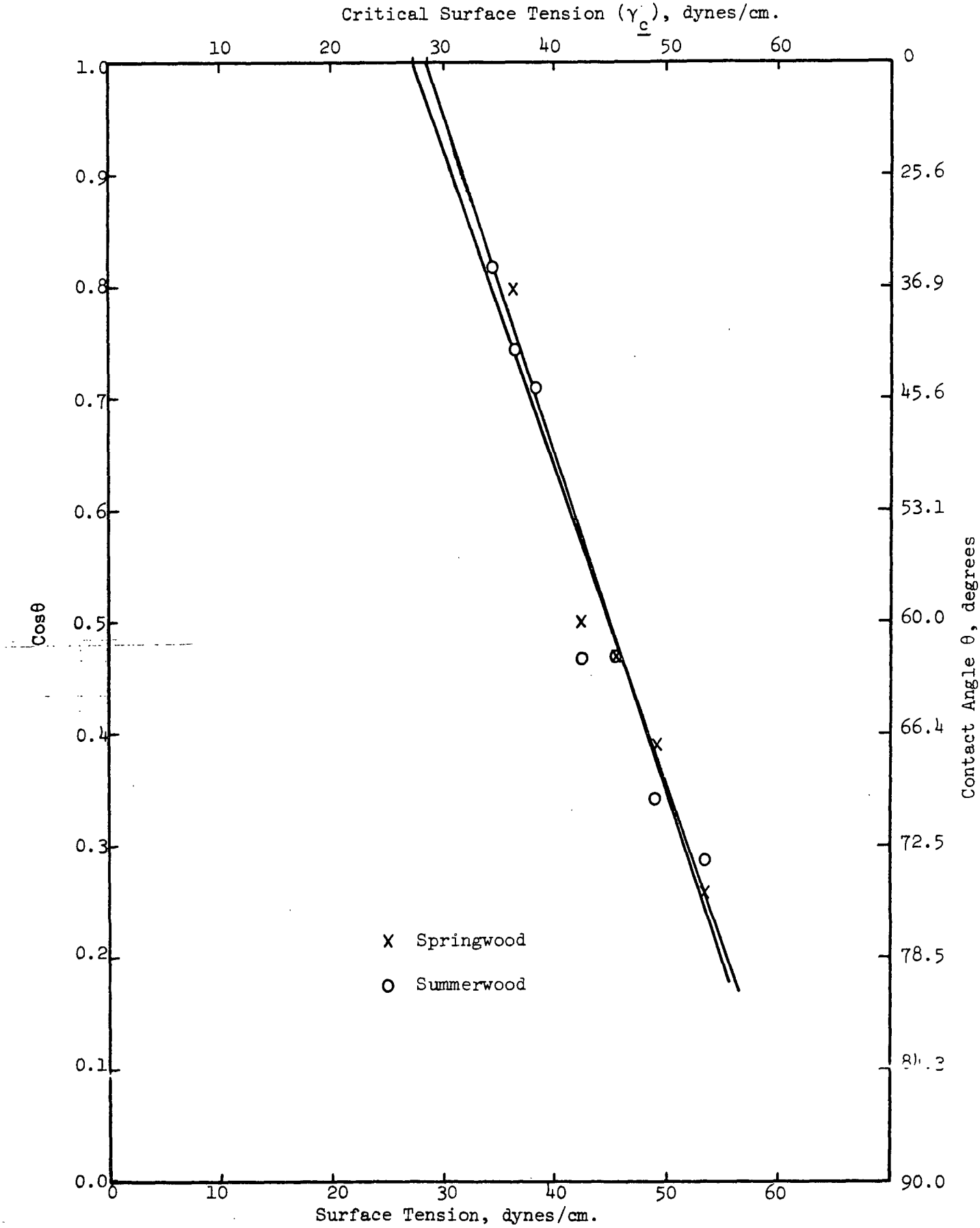

Figure 8. Cosθ — Surface Tension Relationships for Southern Pine Veneer Surfaces Aged 360 Hours (15 Days)

Summary plots for springwood and summerwood are shown in Fig. 9 and 10. Critical surface tension as a function of aging of the veneer surface is recorded in Table II and is plotted in Fig. 11.

TABLE II

THE CRITICAL SURFACE TENSION OF FRESHLY GENERATED AND AGED SOUTHERN PINE VENEER

Aging Time, hr.	γ_c, dynes/cm.	
	Springwood	Summerwood
0	39.3	39.1
4	33.5	35.4
8	35.4	32.3
16	33.5	30.5
48	33.0	32.8
96	31.1	27.5
264	29.5	27.2
360	28.5	27.2

Preparation and Testing of Plywood Layups

Panels of the southern pine veneer were cut into 6 x 6-inch samples and conditioned at 73°F. and 50% R.H., resulting in a moisture content of 8%. The samples were sorted and only those free of cracks, grooves, and other irregularities were selected for testing. On this basis, only 10-20% of the samples were retained. The samples were sanded in two steps according to procedures supplied by PMRL. This consisted of sanding by hand in a circular motion 150 times with a No. 36 sandpaper, followed by another 150 cycles with a No. 120-weight sandpaper. Only those sides of the samples were sanded which would ultimately contact the adhesive, i.e., the open sides of the top and bottom

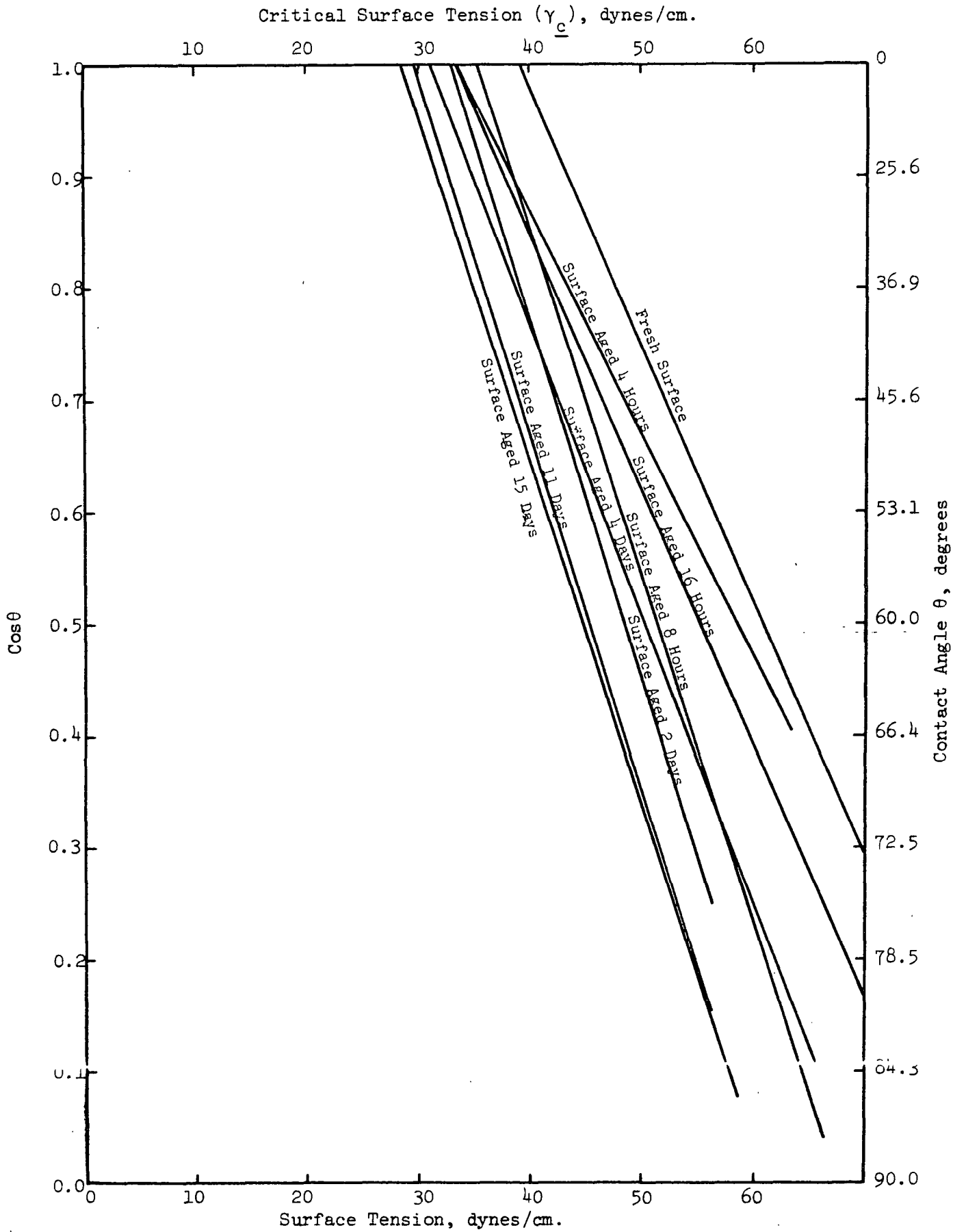

Figure 9. Cosθ — Surface Tension Relationships for Southern Pine Springwood

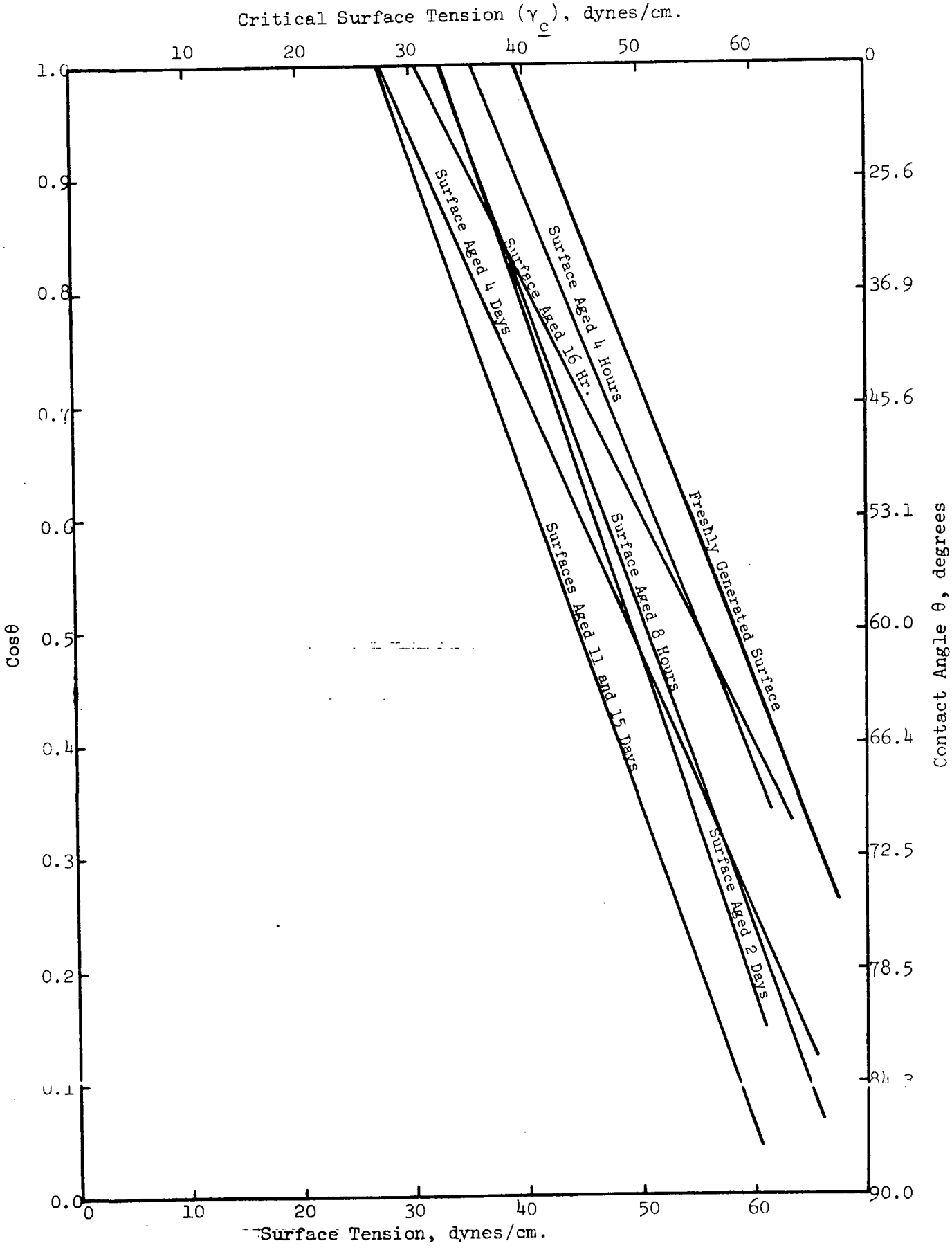

Figure 10. Cosθ — Surface Tension Relationships for Southern Pine Summerwood

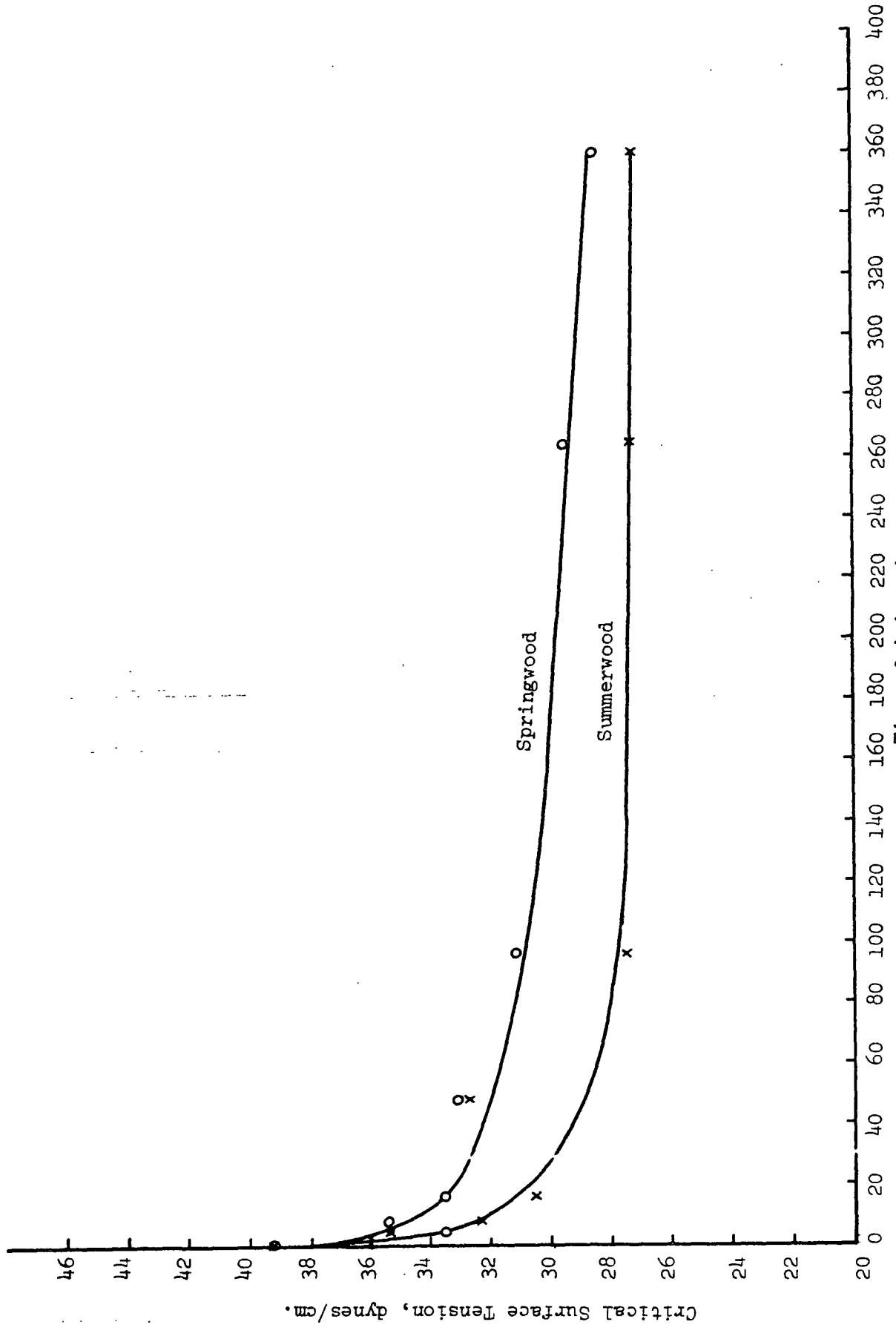

Figure 11. The Effect of Aging on the Critical Surface Tension of Southern Pine Veneer

veneer and both sides of the core veneer (the open side of the veneer is that toward the center of the log).

Two series of layups were made utilizing ELSA (Run 38, 66-2). The first of these utilized the unmodified ELSA at 40% solids; the second utilized a formulated adhesive comprised of 200 g. of 30% ELSA, 48 g. of 50% phenol-formaldehyde resin (CR-9357, Catalin Corp. of America), and 30 g. of 200-mesh wood flour. The phenol-formaldehyde resin was stirred into the 30% ELSA for seven minutes with a glass stirring rod. The mixture was then transferred to a Kitchen Aid mixer, the wood flour added, and the mixture stirred for ten minutes at low speed. The Brookfield viscosity and pH of the formulated adhesive were measured at 27°C. The viscosity and pH of the unmodified ELSA were measured at 23°C.

The veneer surfaces used in making layups included freshly sanded surfaces and surfaces aged 2 and 14 days at 73°F. and 50% R.H. after sanding. Four grams of adhesive were uniformly applied to both sides of the core veneer with a 1/2-inch brush. The adhesive was applied first to the closed side of the core which was then turned over and supported on pins while the adhesive was applied to the other side. The layup was formed immediately by placing the core veneer, open side down on the open side of the bottom veneer. The open side of the top veneer was then placed on the core veneer. The grain direction of the core veneer was placed at right angles to the grain direction of the top and bottom veneer. The layup was then placed on a flat surface under a load of approximately five pounds. A timer was set for five minutes and a second layup was prepared in the same manner. The second layup which required two to three minutes to prepare was placed on top of the first and the stack of two was left under the 5-lb. load for the remainder of the 5-min. stand time. The layups were then pressed in a Carver steam-heated hydraulic press for a given time interval

at 200 p.s.i. and 300°F. The press time was 30 minutes for unmodified ELSA and 4 minutes for the formulated adhesive. After the pressing cycle, the layups were stacked and allowed to cool overnight at room temperature.

The layups were subsequently trimmed and cut into 1 x 2 7/8-inch strips (outer veneer grain long) for tensile shear tests. Each test strip was kerfed 2/3 the distance through the core; one kerf on each side of the specimen separated by exactly one inch. Ten test strips were cut from each 6 x 6-inch layup and the tensile shear strength of each specimen was determined on an Amsler tester. In addition to the numerical results, the test specimens were examined under low-power magnification for the predominant type of failure, i.e., within the wood, at the wood-adhesive interface, or within the adhesive. These results, along with pertinent surface tension and viscosity data, are recorded in Table III. Ruptured veneer surfaces bonded with unmodified ELSA are shown in Fig. 12 and 13. Surfaces bonded with the formulated adhesive are shown in Fig. 14-17.

DISCUSSION OF RESULTS

The results in Tables I and II and Fig. 1-11 confirm the tendency for the critical surface tension (γ_c) of southern pine veneer to decline with aging and, as reported by Herczeg (2), summerwood tends to be of lower γ_c than springwood. The decline in γ_c was rather rapid, initially falling from a level of 39-40 dynes/cm. down to 29-32 dynes/cm. after two days. This was followed by a further decline to 27-29 dynes/cm. after two weeks. On the basis of the chemical theory of adhesion, a lignosulfonate adhesive should have a liquid surface tension of 27-29 dynes/cm. to wet the aged pine surface. Subsequent bonding strength values utilizing unmodified ELSA with a liquid surface tension of 43.9 dynes/cm. and a formulated adhesive with a surface tension of 44.6 dynes/cm. showed considerable variability (Table III)

TABLE III

THE BONDING STRENGTH OF SOUTHERN PINE PLYWOOD UTILIZING ELSA AND FORMULATED ADHESIVE

Adhesive	Surface Tension of Adhesive (γ_L), dynes/cm.	Viscosity of Adhesive, cp. (Brookfield, 12 r.p.m.)	pH of Adhesive	Age of Veneer Surface, days	Critical Surface Tension of Veneer Surface (γ_C), dynes/cm.	Bonding Strength, lb./in.	Average	Standard Deviation	Predominant Type of Failure, approx. %
ELSA									
No. 66-2, Run 38	43.9	39.5	0.6	0	39.2	179.6			
						145.9			
						127.4			
						53.9			
						86.1			
						81.2			
						122.3			
						51.8	106.0	±45.3	Cohesional (within adhesive), 80
				2	30.5	150.1			
						155.2			
						101.0			
						122.9			
						93.1			
						102.3	120.8	±26.6	Cohesional, 80
				14	27.9	93.3			
						16.1			
						90.9			
						115.7			
						109.3			
						67.9	82.2	±36.4	Cohesional, 90
Formulated adhesive	44.6	667.5	0.7	0	39.2	201.7			
						220.6			
						293.0			
						191.7			
						202.7	221.9	±41.1	Within wood, 70-90
				2	30.5	180.8			
						186.5			
						203.3			
						254.5			
						231.4	211.3	±31.1	Within wood, 60-90
				14	27.9	209.6			
						177.9			
						218.9			
						191.0			
						180.4			
						259.4	206.2	±30.7	Within wood, 50-80

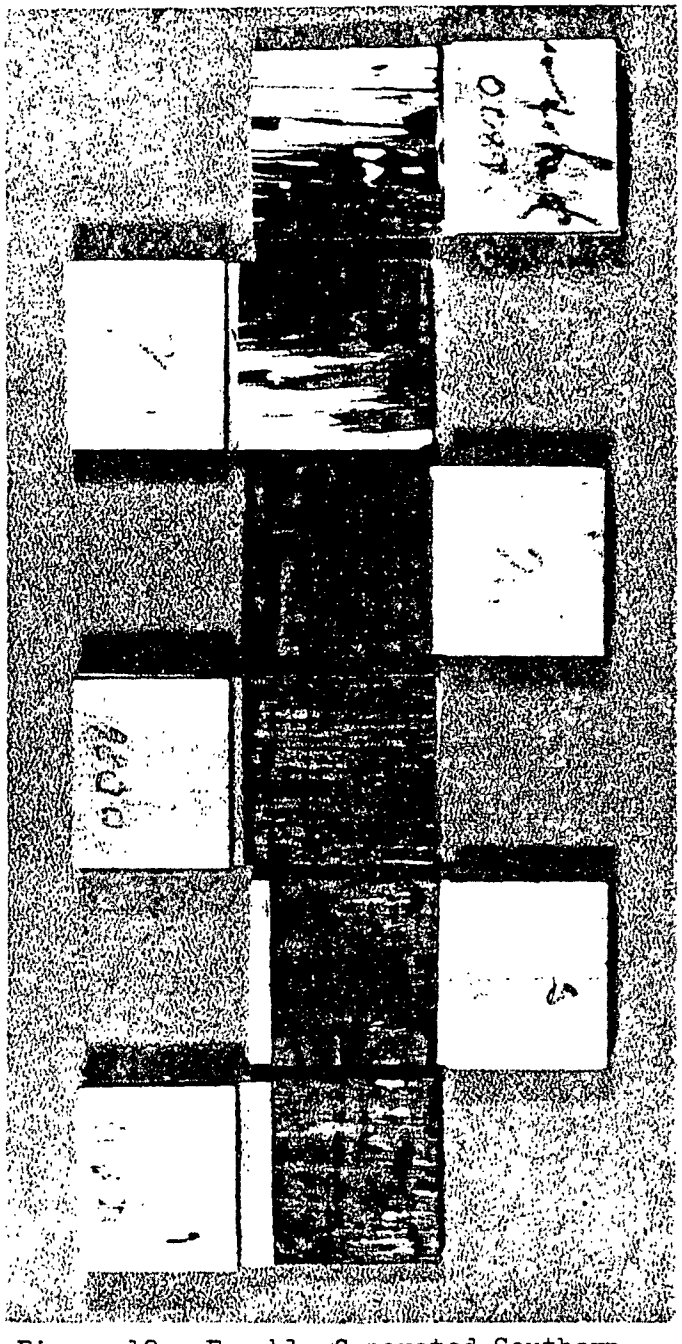

Figure 12. Freshly Generated Southern Pine Veneer Surfaces Bonded with Unmodified ELSA Adhesive

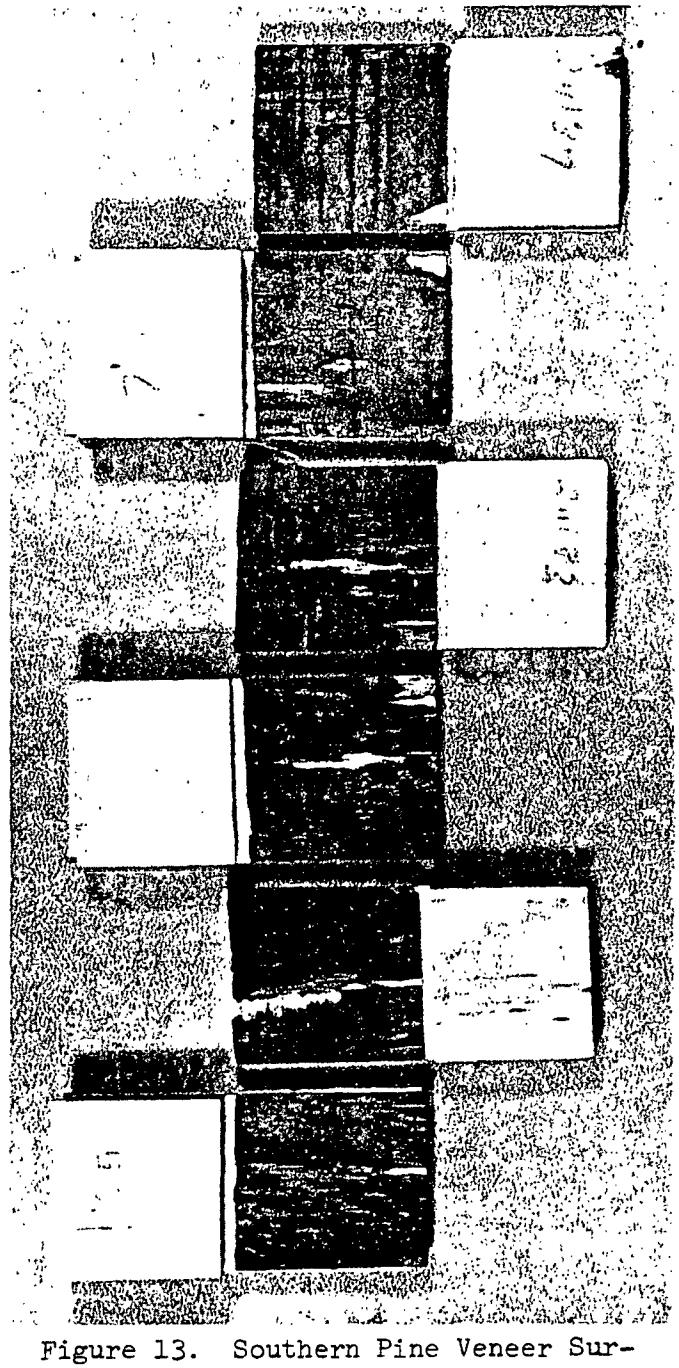

Figure 13. Southern Pine Veneer Surfaces Aged Two Weeks and Bonded with Unmodified ELSA Adhesive

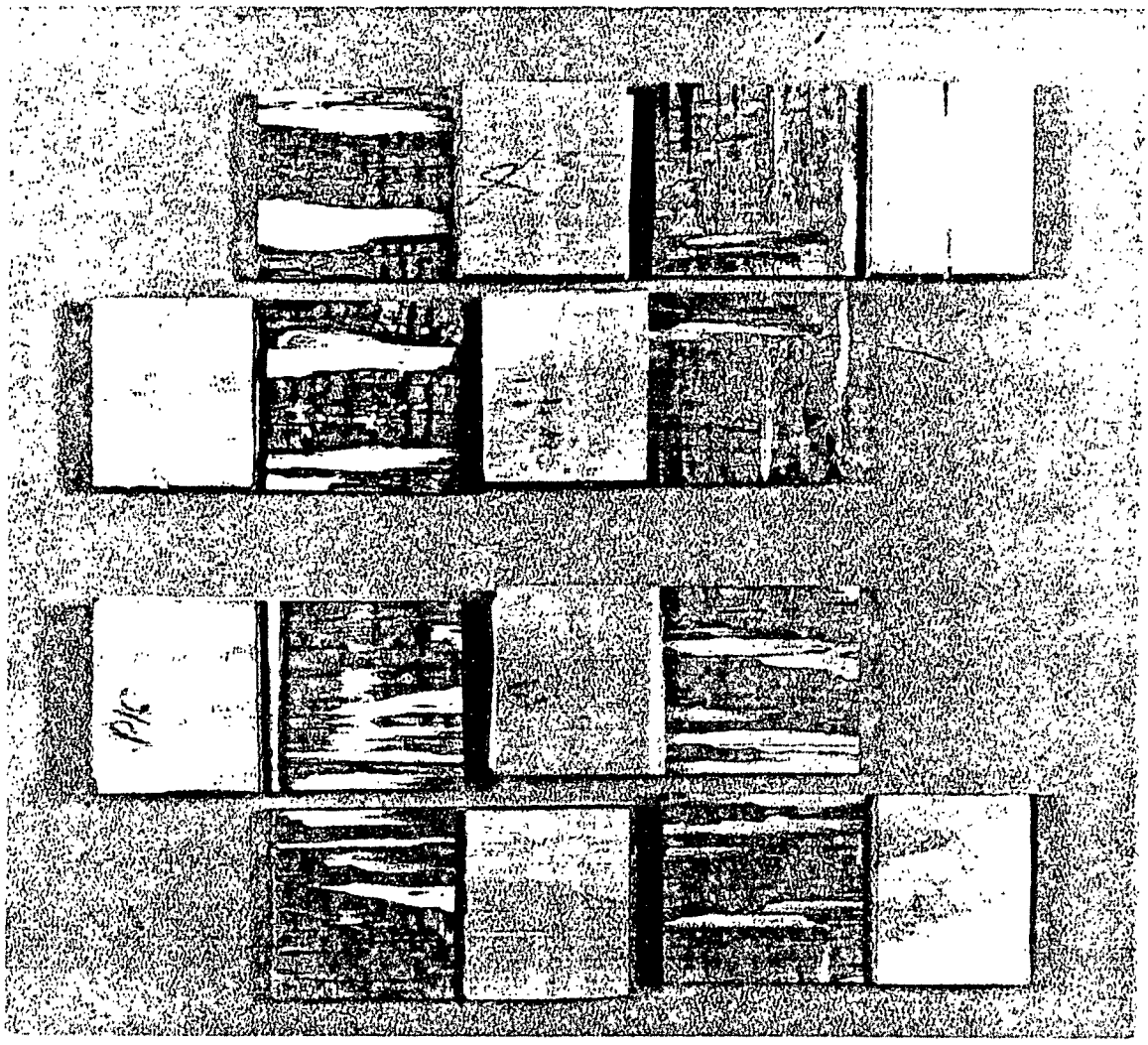

Figure 14. Freshly Generated Southern Pine Veneer Surfaces Bonded with Modified ELSA Adhesive

Figure 15. Freshly Generated Southern Pine Veneer Surface Bonded with Modified ELSA Adhesive — Approx. 5X

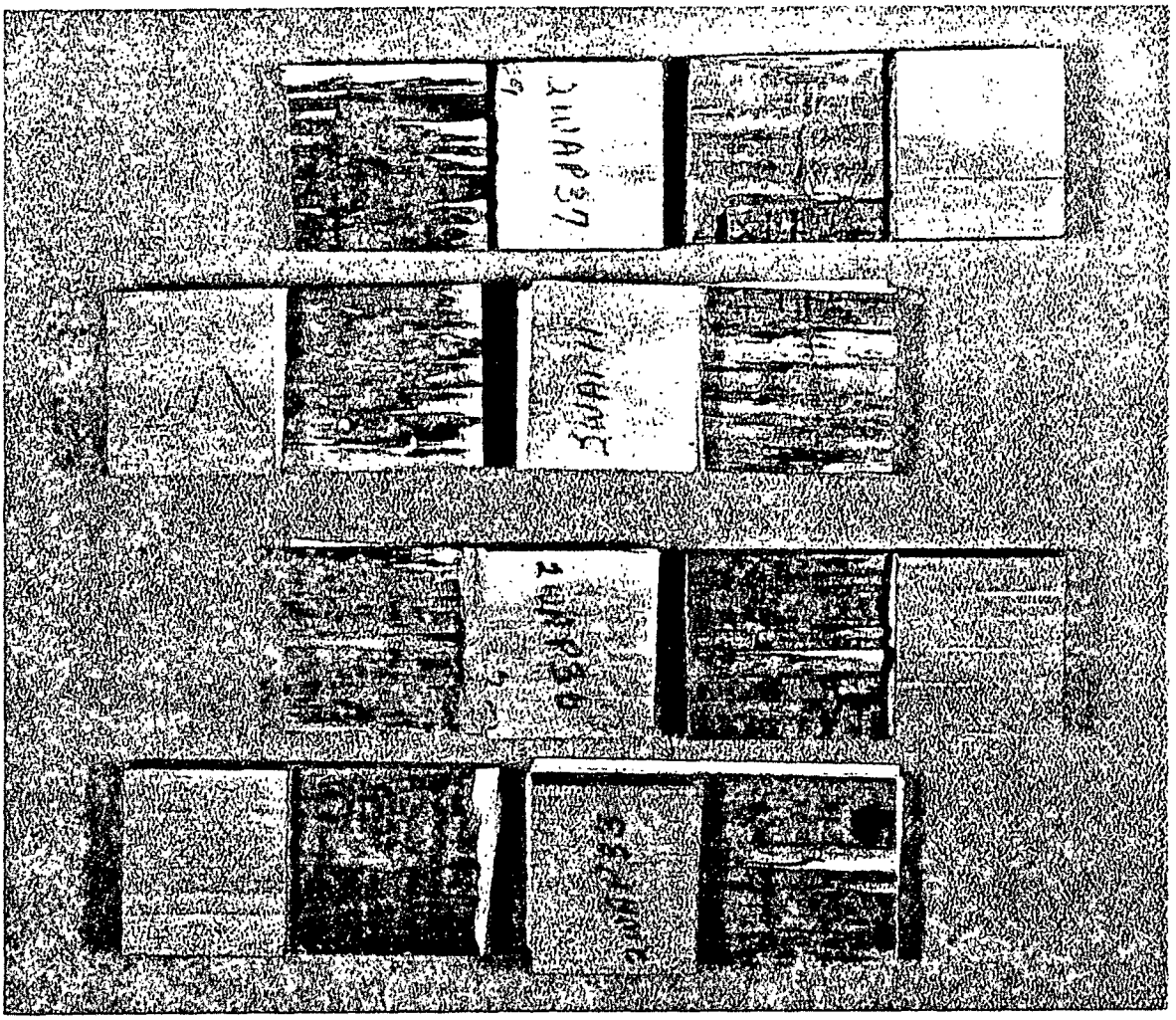

Figure 16. Southern Pine Veneer Surfaces Aged Two Weeks and Bonded with Modified ELSA Adhesive

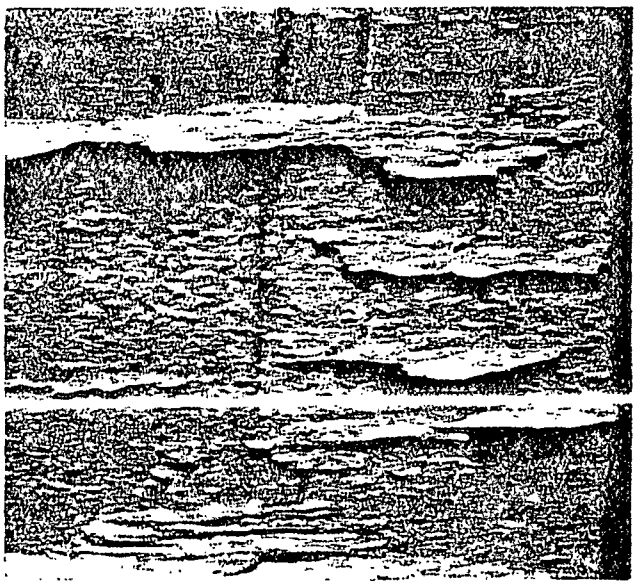

Figure 17. Southern Pine Veneer Surface Aged Two Weeks and Bonded with Modified ELSA Adhesive — Approx. 5X

and, while a trend for reduced strength in the 2-week aged surfaces was indicated, statistical treatment of the results failed to show a real difference within a given series. Strictly speaking, the liquid surface tension of the adhesives was 4-5 dynes/cm. higher than γ_c of the freshly generated surfaces and about 15 dynes/cm. higher than γ_c of the 2-week aged surfaces. On this basis, incomplete wetting of the surfaces and relatively poor adhesion would be expected. However, the layups are formed under pressure which forces adhesive into the numerous surface irregularities prevalent in wood, particularly southern pine. This results in some mechanical anchoring which assists bonding provided the cohesive strength of the adhesive is adequate. Inspection of the ruptured specimens under low-power magnification revealed that failure in layups bonded with unmodified ELSA was approximately 80-90% cohesional, i.e., the failure occurred within the adhesive leaving a layer on both surfaces of the ruptured joint (Fig. 12 and 13). Only 5-20% of the failure in these specimens occurred within the wood. It was noted, however, that more wood failure, or, in other words, better adhesion, generally occurred among samples formed from freshly generated surfaces than from aged surfaces. This observation is in keeping with the measured differences in the critical surface tension and with practical bonding experience. In contrast, layups bonded with the formulated adhesive showed roughly twice the bonding strength, 50-90% wood failure, and a much lower level of cohesional failure (Fig. 14-17). Effective adhesion was sometimes shown to be higher than casual inspection of the surfaces would indicate. This is indicated in Fig. 15 and 17 which show thin or discontinuous layers of wood pulled from one or both surfaces. Once again, freshly generated surfaces tended to show more wood failure than the aged surfaces.

It was observed in both series of tests that the most obvious wood failure generally occurred in the springwood. Failure in the summerwood was less pronounced

or at least less obvious. This effect presumably results from the poorer wettability and penetrability of the summerwood.

In a sense, the predominant type of failure was cohesional in both series of layups, i.e., within the adhesive in the case of the unmodified ELSA and within the wood in the case of the formulated adhesive. In other words, poor adhesion was not a predominant cause of failure. The fact that the percentage of wood failure was as high as 90% in some cases would leave little margin for improvement. However, since the aged surfaces tended to show slightly lower bonding strength and less wood failure, some room for improvement is indicated. Herczeg (2) in his work with Douglas-fir showed that the maximum bonding strength from a urea resin was attained at a liquid surface tension of 49.6 dynes/cm. when the critical surface tension of the wood surface ranged from 44-50 dynes/cm. (summerwood and springwood). Reducing the surface tension of the adhesive with a surfactant to 38.7 dynes/cm. caused a noticeable loss in bond strength. Hence, the optimum bonding strength was obtained under conditions where the adhesive displayed a very low contact angle or was just able to spread on the wood surface. This agrees in part with Zisman's (3) work which shows that the maximum work of adhesion generally occurs at a low but finite contact angle. On this basis, the surface tension of the lignosulfonate adhesive should be in the order of 30-35 dynes/cm. for optimum bonding strength in aged southern pine plywood.

FUTURE WORK

Future work in the adhesional phase of the project will be directed at modification of the ELSA adhesive to provide a lower surface tension and improved bonding in southern pine plywood. In accordance with the discussion presented in the previous section, a surface tension range of 30-35 dynes/cm. will be explored.

This will likely be accomplished through incorporation of selected surface-active agents or the low molecular weight ELSA fraction described in Progress Report Seven. Surface-active agents selected for this purpose must be stable at very low pH (0.6-0.7), they must provide the desired surface tension at very low concentration, and they must not stabilize foam under the conditions employed. Several exploratory tests have already been made with an anionic and a cationic surface-active agent. Both of the agents examined were stable in sulfuric acid at pH 0.6 and were effective in reducing surface tension to 30-35 dynes/cm. at a concentration of approximately 0.01%. However, when added to ELSA or the formulated adhesive, 0.1-0.2% was needed to produce the same surface tension level. When utilized in the ELSA adhesives at this concentration bonding strength was either weakened or unaffected. It was assumed that the surfactant interacted with, or was adsorbed by, the ELSA adhesive. Future efforts with surfactants will be directed primarily at the utilization of nonionics. A number of these are ethers which should be stable at low pH and should be relatively inert.

MECHANICAL PROPERTIES OF LIGNOSULFONIC ACIDS

INTRODUCTION

The ability of an adhesive to withstand an applied stress depends upon stress distribution within the adhesive. Internal stress redistribution is accomplished through molecular relaxation, a property which is manifest in the viscomechanical behavior of the adhesive (4). The most convenient measure of this relaxation is the loss tangent, which is the ratio of energy lost to energy stored in a periodic application of stress (i.e., the ratio of the imaginary to the real component of the complex modulus of the viscoelastic material).

It is the goal of the cohesional phase of this project to relate the viscomechanical properties of lignosulfonic acid materials to their adhesive strength, particularly in plywood operations. Greater understanding of the relationship will aid significantly the development of adhesive formulations.

The work previously reported (5) indicated that the vibrating reed technique of measuring viscomechanical properties, including the loss tangent, was potentially adaptable to plywood adhesive studies. Although there was an adhesion problem with aluminum and glass surfaces, wood veneer was easily bonded and reed data were obtainable. The real Young's modulus (solidlike behavior) showed no evident relationship to the estimated bond strength. However, the loss tangent of the reed was controlled too much by the relatively massive wood substrate for the adhesive behavior to be evident. It is the purpose of the present work to (1) test the possibility of removing low molecular weight, potentially low surface energy orienting molecules from the lignosulfonate materials to improve their wettability, and (2) to find lighter weight substrates suitable for obtaining useful loss tangent data.

EXPERIMENTAL

Ether Extraction of Electrodialyzed Lignosulfonic Acid

In an effort to remove low molecular weight, surface orienting molecules, a 25-ml. sample of 65-24-R44 (a heat-treated, sodium-based ELSA), 38% solids was placed in a 250-ml. separatory funnel. To this were added 100 ml. of reagent-grade ethyl ether. The mixture was agitated manually at the end of each of three 5-min. intervals. The aqueous and ether phases were then separated and placed in glass-stoppered bottles for storage.

Substrate Preparation

The materials for potential use as substrates for reeds were examined for adhesive wettability. The substrate was scrubbed with an Alconox (Alconox Inc., New York) detergent solution, rinsed with tap water, and rinsed finally with distilled water. In some cases, as noted, the substrate was further rinsed with reagent-grade ether.

A drop or two of the ether-extracted ELSA or the higher molecular weight fractions from a gel permeation fractioned ELSA [Fractions 2421-3-1, 2421-3-2, 241-3-3, described in Progress Report Seven (1), which are the first three fractions of Sample 66-2-R38, an ammonium-base ELSA] were placed on the substrate at room conditions of temperature and humidity and allowed to dry for several days. Visual observation was then made for evidence of cracking and release.

Reed Preparation and Vibrational Measurements

Layups of substrate and adhesive were prepared by applying adhesive to two 6 x 6-inch sheets of substrate, placing them face to face, and curing this sandwich between platens heated to 310°F. for 30 min. at 150 p.s.i. The sandwich was backed top and bottom first with 0.015-inch aluminum foil, and next with 1/8-inch fir veneer

when in the platens. When applying the adhesive with a rod, a uniform rapid motion was required while applying some finger pressure to the center of the rod so that it would not bow. Table IV lists the substrates initially examined using 65-24-R44 ELSA.

Using the kraft paper substrate, 6 x 6-inch layups were made in a like manner employing the following adhesives:

(1) Ether extracted 65-24-R44

(2) Heat concentrated 65-24-R44

(3) 67-36-R2, an ammonium-base, whole liquor, 39% solids

(4) 66-2-R38, an electrodialyzed, ammonium base, whole liquor, 40% solids. (For 30% solids the Brookfield viscosity at 25°C. and 12 r.p.m. is 4.0 centipoise.)

(5) Phenol-formaldehyde resin, 50% solution, CR 9357, Catalin Corp. of America, Chicago, Illinois. (The Brookfield viscosity at 22°C. and 12 r.p.m. is 4.7 centipoise.)

(6) Best formulation of Holderby, Olson, and Wegener (6); 30% ELSA solids (Sample 66-2-R38 used here) — 100 parts, 50% phenol-formaldehyde — 24 parts, 200-mesh wood flour — 15 parts, freshly prepared and used immediately. (The Brookfield viscosity at 27°C. and 12 r.p.m. is 450 centipoise.)

Reeds, 2.0 x 0.25 inch and 6.0 x 0.25 inch were cut from each layup from the locations indicated in Fig. 18, using a guillotine paper cutter. In the case of the glass fiber filter disks, the 2.0 x 0.25-inch reed was cut from the center region of the disk layup.

TABLE IV

LAYUPS WITH VARIOUS SUBSTRATES AND ADHESIVES CURED AT 310°F. FOR 30 MIN. AND 150 P.S.I.

Substrate	Adhesive	Weight of 6x6 in. Layup Without Adhesive, g.	Weight of Layup with Adhesive, after curing, g.	Weight of Adhesive in Layup, g.	Coating Rod
Red gasket rubber	65-24-R44	61.1330	61.3505	0.2175	Glass
Mylar	65-24-R44	12.3690	12.6421	0.2731	Mayer, No. 8
Fiber glass filter[a]	65-24-R44	1.3173	1.7348	0.4175	--
Kraft paper[b]	65-24-R44	9.7602	9.9804	0.2202	Mayer, No. 10
Kraft paper	65-24-R44	9.6650	9.9815	0.3165	Mayer, No. 14
Kraft paper	65-24-R-44-ether extracted	9.7623	9.9342	0.1719	Mayer, No. 12
Kraft paper	66-2-R38	9.6173	9.9847	0.3674	Mayer, No. 10
Kraft paper	67-36-R2	9.6757	10.0828	0.4071	Mayer, No. 12
Kraft paper	Phenol-formaldehyde	9.7384	10.3317	0.5933	Mayer, No. 8
Kraft paper	ELSA-phenol-formaldehyde wood flour formulation	9.6651	10.3898	0.7247	Mayer, No. 14

[a]Consisting of eight fiber glass filter disks, 5.5 cm. in diameter, coated by soaking each in the adhesive making four face to face pairs in the layup.

[b]Linerboard, 210 g./M^2 or 149 lb./TAPPI ream.

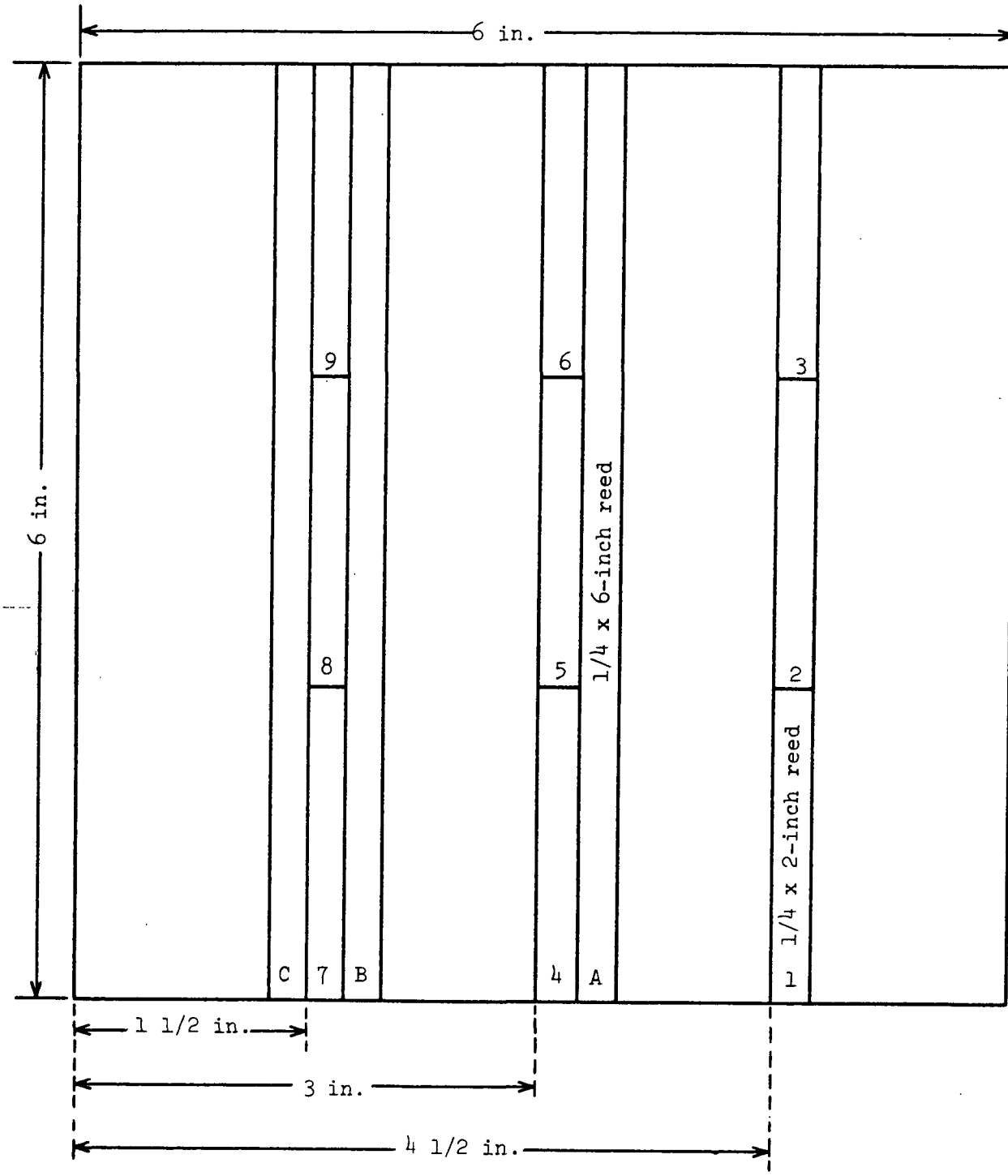

Figure 18. Location of Reeds Cut from a 6 x 6-Inch Layup

The vibrational measurement of the reeds were obtained as described in Progress Report Eight (5) by use of an audiooscillator coupled through an amplifier to a magnetic recording head (Astatic type M 41-8) of the type used in the cutting of phonograph records. The recording needle was replaced by a lightweight clamp consisting of a Cook's No. 2 file signal which was silver soldered to a 5/8 x 0.037-in. diameter stainless steel pin, as described by Riemen and Kurath (7). The file signal is a convenient clamp for paper reeds. The weight of the clamp is approximately 0.6 g. The resonance frequency of the unloaded clamp when mounted in the recording head is above 1000 c.p.s. for a typical clamp assembly.

A potential of 3.6 volts was applied to the recording head. The reed vibrational amplitude was measured by means of a traveling telescope. The resonance frequency, ω_o and resonance band width, $\Delta\omega$ at $1/\sqrt{2}$ of the maximum vibrational amplitude were determined by the two point method as described in Progress Report Eight (5).

RESULTS AND DISCUSSION

In an effort to increase the influence of the adhesive on the viscomechanical properties of the reed and thereby acquire data on the loss modulus of the adhesive, lighter materials than wood for substrate use were examined. Listed in Table V are the results of substrate evaluation for wettability using an ELSA, an ether-extracted ELSA, and several high-molecular weight fractions of an ELSA. As the wettability behavior of whole and extracted or fractionated ELSA is about the same, the loss of wettability on drying is apparently not due to orientation behavior of low-molecular weight, low-surface energy molecules. Only the substrates which were porous or with great surface roughness gave apparent continued adhesion with drying sufficient for reed work.

TABLE V

SUBSTRATE EVALUATION OF WETTABILITY

Substrate	ELSA Sample[a]	Results[b]
Aluminum	Whole	Cracked and released
	Ether extracted	" " "
	2421-3-1	" " "
	2421-3-2	" " "
	2421-3-3	" " "
Glass	Whole	" " "
	Ether extracted	" " "
	2421-3-1	" " "
	2421-3-2	" " "
	2421-3-3	" " "
Etched glass	Whole	Cracked and adhered depending on humidity
	2421-3-1	Cracked and adhered
	2421-3-2	" " "
	2421-3-3	" " "
Cellulose acetate	2421-3-2	Cracked and released
Dacron cloth	2421-3-2	Soaked into fabric
Nylon cloth	2421-3-2	" " "
Fiber glass filter	Whole	Soaked into fabric and stiffened it
	Ether extracted	" " " " " "
	2421-3-2	" " " " " "
Papylon (vinyl fiber mats)	Whole	Soaked into fabric
	2421-3-2	" " "
Millipore filter	2421-3-2	" " "
Polyolefin cloth	2421-3-2	" " "
Cellophane (unplasticized)	Whole	Cracked and partially released
	2421-3-2	" " " "
Mylar	Whole	" " " "
	Ether extracted	" " " "
	2421-3-2	Cracked and released
Fiber glass cloth	Whole	Wetted and adhered
	Ether extracted	" " "
	2421-3-2	Cracked and adhered
Garlock gasket	2421-3-2	" " "
Johns Manville asbestos gasket	2421-3-2	" " "
Red rubber gasket (1/32 in.)	Whole	Cracked and partially adhered
	Ether extracted	" " " "
	2421-3-2	Cracked and adhered
Black rubber gasket (1/16 in.)	2421-3-2	" " "
Black rubber gasket (1/32 in.)	2421-3-2	Cracked and released
Kraft paper (210 g./M^2)	Whole	Wetted and adhered
	Ether extracted	Wetted and adhered with some penetration
	2421-3-2	" " " " " "

[a]The whole and ether extracted refer to 65-24-R44, a sodium-base, heat-treated, ELSA and 2421-3-1, -2, and -3 refer to the first three fractions from gel permeation chromatography of 66-2-R38 (1).

[b]The extent of adherence was found to depend on humidity with best wettability under highest humidity and no wettability in ovendry state.

Because of the partial wettability success, red rubber gasket, Mylar, fiberglass filter, and kraft paper were examined for reed behavior. The results are listed in Table VI. Besides the undesirable vibrating characteristics of the red rubber, partial ply separation was observed. The bonding in the Mylar reed was very poor, which is confirmed by noting that there is essentially no change in ω_o from the single ply reed to the adhesive reed. The kraft paper was selected over the fiberglass mat for further reed work because of its lower loss tangent and its similarity to wood. The adhesives previously examined (5) were tested again along with the ether-extracted 65-24-R44 and the heat-concentrated 65-24-R44. The results are included in Table VI. The basic data for these reed measurements can be found in Appendix II.

The average Young's modulus of the reeds (see Appendix I for a sample calculation) is twofold higher than that of the kraft paper, indicating that the ELSA materials and the phenol-formaldehyde have Young's moduli greater than 5×10^{10} dynes/cm.^{2} This is consistent with the earlier work reported on the wood reed study.

The formulation and the phenol-formaldehyde are good adhesives and, as anticipated, have the highest average loss tangent. However, the range of values from paper only to the best bonded reed is small (0.024-0.050) and the scatter about each average is high (up to $\pm$ 50%) so that valid trends are not yet possible to discern. [These loss tangent values are of the same magnitude as those found by Riemen and Kurath (7) for bleached sulfite paper.] By using lighter weight paper it may be possible to increase the sensitivity of the adhesive to the measured loss tangent. It is interesting to note that the loss tangent of the loosely bonded glass fiber mat decreased significantly with the addition of ELSA adhesive, indicating a reduced tendency to deform under stress. This is probably a result of increased fiber-fiber bonding in the ELSA soaked mat.

TABLE VI

VIBRATING REED DATA

Adhesive[a]	Substrate	Reed Number (Fig. 1)	Reed Length, in.	ω, c.p.s.	Av.[g] Δω, c.p.	Young's Modulus, E',[c] dynes/cm.^{2}	Loss Tangent, E"/E'=Δω/ω		Surface Tension,[d] dynes/cm.
None-one ply reed	Rubber[e]	--	2	16.40	1.85	--	0.113		--
" " " "	Mylar	--	2	26.80	0.90	--	0.033		--
" " " "	Fiber glass	--	2	16.65	1.73	--	0.074		--
" " " "	Kraft[b]	--	2	33.80	0.80	2.7×10^{10}	0.024		--
65-24-R-44	Rubber[e]	1	2	31.50	--	--	--		--
"	"	6	2	--	--	--	--		--
"	Mylar	5	2	27.50	0.75	--	0.020		--
"	Fiber glass[f]	--	2	41.80	1.00	--	0.024	0.029	--
"	" "	--	2	40.50	1.35	--	0.033		
"	Kraft	1	2	86.50	2.80	4.6×10^{10}	0.032		
"	"	5	2	78.00	1.55	4.2	0.016	0.025	50.3
"	"	9	2	79.20	2.30	3.9	0.028		
65-24-R-44-ether extracted	"	1	2	101.50	3.00	6.8×10^{10}	0.030		
"	"	5	2	87.40	3.55	5.4	0.041	0.035	54.6
"	"	9	2	96.00	3.30	8.0	0.034		
65-24-R-44-heat concentrated	"	1	2	102.40	--	7.3×10^{10}	--		
"	"	5	2	92.20	2.70	7.2	0.029		
"	"	9	2	95.30	--	6.0	--	0.041	--
"	"	A	6	11.40	0.57	6.5	0.050		
"	"	B	6	10.31	0.45	5.3	0.043		
67-36-R-2	"	1	2	97.20	3.70	6.4×10^{10}	0.038		
"	"	5	2	93.80	3.45	5.9	0.037	0.034	(40.8)
"	"	9	2	94.00	2.50	5.4	0.027		
66-2-R-38	"	1	2	89.80	2.70	5.4×10^{10}	0.030		
"	"	5	2	86.20	4.55	4.9	0.053	0.038	45.5
"	"	9	2	81.70	2.45	5.2	0.030		(43.6)
R-38, Phenol formaldehyde, wood flour formulation	"	1	2	96.30	5.15	7.3×10^{10}	0.053		
	"	5	2	92.00	3.70	5.3	0.040	0.045	42.9
	"	8	2	91.40	3.85	5.2	0.042		
Phenol formaldehyde	"	1	2	97.30	4.35	7.8×10^{10}	0.045		
" "	"	5	2	95.20	3.05	7.4	0.032		
" "	"	9	2	97.10	--	5.2	--	0.050	56.7
" "	"	A	6	10.82	0.87	5.5	0.079		
" "	"	B	6	11.00	0.45	6.0	0.041		
" "	"	C	6	11.68	0.62	6.7	0.053		

[a] See page 30 for adhesive descriptions.
[b] Kraft paper, 210 g./M^2 (149-lb. per TAPPI ream).
[c] See Appendix I for method of calculation.
[d] Values in parentheses are from Progress Report Seven (5).
[e] Waves visible in reed under vibration indicating complex vibrational behavior.
[f] The reeds were cut from the 5.5 cm. diameter two-ply disks.
[g] The average from measuring the band width when viewing the reed from the right side and from the left side. The scatter is up to ± 50% (see Appendix II).

Surface tensions of the adhesives were also determined with a DuNouy tensiometer and are included in Table VI. It is significant to note that phenol-formaldehyde has the highest value, 56.7 dynes/cm. Considering the much lower critical surface tension of wood surfaces, bonding may be accomplished at least in part by mechanical linkages (adhesive penetration of the porous structure). Improvement of wetting may improve adhesive performance. It is interesting to note that ether extraction significantly increased the surface tension as expected. Also note that the formulation has a surface tension lower than either adhesive component, perhaps through the effect of the added wood flour.

FUTURE WORK

In order to make the loss tangent of the reeds more sensitive to the adhesive behavior, lighter weight paper will be examined for reed construction. Methods of measuring the adhesive strength will be considered and applied to the reed system. The relationship of loss tangent to adhesive strength will thus be examined.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Messrs. Gerald R. Hoffman and Norman L. Colson for their help in much of the experimental work presented in this report. Appreciation also goes to Mr. Jesse M. Holderby and Dr. John W. Collins of Pulp Manufacturers Research League for their many helpful discussions and to the League staff for their help in preparing the adhesive formulation.

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APPENDIX I

CALCULATION OF YOUNG'S MODULUS OF THE VIBRATING REED

From the development given in Progress Report Eight, the Young's modulus is related to the vibrational frequency of a reed by the equation

$$E' = [(12)/(1.875)^4](\rho \ell^4/a^2)\omega_o^2$$

where ρ is the density of the reed, ℓ and a are the length and thickness of the reed, and ω_o is the resonance frequency at which the free end of the reed is a maximum. Selecting as an example the single-ply kraft paper reed (see Appendix II, Table VII)

$$E' = [(12)/(1.875)^4][(0.735)(2.000 \times 2.540)^4/(0.011 \times 2.540)^2](2\pi \times 33.8)^2 = 2.72 \times 10^{10}$$

APPENDIX II

VIBRATING REED DATA

Listed in Table VII are the basic data of the reeds discussed in this report and used in the preparation of the results listed in Table V.

TABLE VII

BASIC VIBRATING REED DATA

Adhesive	Substrate	Reed No.	Reed Dimensions, in.			Reed Mass, g.	ω_o, c.p.s.	Maximum Vibrational Amplitude, cm.	Band Width, $\Delta\omega$, c.p.s.	
			Length	Width	Thickness				Left Edge View	Right Edge View
None-one ply reed	Red rubber	--	2	--	--	--	16.4	0.1434	1.90	1.80
" " " "	Mylar	--	2	--	--	--	26.8	0.2432	0.90	0.90
" " " "	Fiber glass filter	--	2	--	--	--	16.7	0.1556	0.95	1.51
" " " "	Kraft paper[a]	--	2.000	--	0.011	--	33.8	0.1462	0.70	0.90
65-24-R44	Red rubber	1	2	--	--	0.7620	31.5	--	--	--
"	" "	6	2	--	--	0.8034	--	--	--	--
"	Mylar	5	2	--	--	0.1501	27.5	0.1660	0.80	0.70
"	Fiber glass filter	C	2 3/16	--	--	0.0688	41.8	0.1183	1.00	1.00
"	" " "	D	2 1/16	--	--	0.0603	40.5	0.2114	1.00	1.70
"	Kraft paper	1	1.998	0.260	0.022	0.1415	86.5	0.1495	2.30	3.30
"	" "	5	2.012	0.245	0.021	0.1295	78.0	0.1491	1.60	1.50
"	" "	9	1.998	0.255	0.021	0.1234	79.2	0.1445	2.40	2.20
Blend, wood flour-R38-	" "	1	1.963	0.250	0.020	0.1383	96.30	0.2115	4.50	5.80
phenol-formaldehyde	" "	5	2.003	0.255	0.022	0.1405	92.00	0.1916	3.50	3.90
" "	" "	8	2.000	0.268	0.022	0.1449	91.40	0.2071	4.50	3.20
65-24-R44-heat	" "	1	1.979	0.260	0.021	0.1424	102.40	0.1924	--	7.30
concentrated	" "	5	1.997	0.250	0.020	0.1409	92.20	0.1995	3.50	2.40
" "	" "	9	1.997	0.232	0.022	0.1354	95.30	0.2237	--	6.80
" "	" "	A	5.960	0.297	0.022	0.4890	11.40	0.3657	0.54	0.60
" "	" "	B	5.950	0.295	0.022	0.4882	10.31	0.3662	0.42	0.47
Phenol-formaldehyde	" "	1	1.980	0.273	0.020	0.1524	97.30	0.1900	4.20	4.50
" "	" "	5	1.992	0.240	0.020	0.1304	95.20	0.1960	3.00	3.10
" "	" "	9	1.997	0.250	0.023	0.1375	97.10	0.2138	--	6.00
" "	" "	A	5.920	0.290	0.022	0.4821	10.82	0.4080	0.75	0.98
" "	" "	B	5.932	0.290	0.022	0.4907	11.00	0.3710	0.44	0.45
" "	" "	C	5.913	0.295	0.022	0.4951	11.68	0.3587	0.61	0.62
66-2-R38	" "	1	1.990	0.248	0.021	0.1299	89.80	0.1939	1.50	3.90
"	" "	5	1.975	0.248	0.021	0.1306	86.20	0.1507	4.60	4.50
"	" "	9	1.977	0.260	0.020	0.1392	81.70	0.2027	2.50	2.40
67-36-R2	" "	1	1.975	0.262	0.021	0.1407	97.20	0.1959	3.70	3.70
"	" "	5	1.990	0.250	0.021	0.1300	93.80	0.1850	3.00	3.90
"	" "	9	1.985	0.262	0.022	0.1439	94.00	0.2006	2.80	2.20
65-24-R44	" "	1	1.983	0.260	0.021	0.1356	101.50	0.1708	3.00	3.00
ether extracted	" "	5	2.000	0.248	0.021	0.1341	87.40	0.2021	3.20	3.90
" "	" "	9	1.993	0.253	0.021	0.1397	96.00	0.1703	3.00	3.60

[a] Linerboard, 210 g./M^2, with density of 0.735 g./$cm.^3$